Magnetic properties of the non-stoichiometric $TbCo_2Ni_x$ alloys

Alexander Inishev*, *Evgeny* Gerasimov, *Nikolay* Mushnikov, *Pavel* Terentev, and *Vasily* Gaviko

M.N. Miheev Institute of Metal Physics UB RAS, Ekaterinburg, Russia
Institute of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia

Abstract. The magnetic and magnetothermal properties of the non-stoichiometric $TbCo_2Ni_x$ ($0 \leq x \leq 0.2$) alloys were studied. It was found that the concentration dependence of the Curie temperature and magnetic moment of the 3d-sublattice have a maximum at $x = 0.025$. The obtained experimental magnetic properties of the $TbCo_2Ni_x$ alloys were discussed under assumption that the Co magnetic moment in the compounds changes with increasing x. The magnetic entropy change was determined using the temperature dependences of the magnetization and Maxwell's thermodynamic relation. The obtained results for $TbCo_2Ni_x$ were compared with those for the $ErCo_2Mn_x$ alloys.

1 Introduction

It was found recently that ternary RM_2Mn (R – rare-earth metal, M – 3d transition metal Ni, Co) compounds crystallize in the Laves-phase $MgCu_2$-type cubic structure in spite of the ratio of the R and M components is 1 to 3. The Mn atoms in Laves-phase structure of the RM_2Mn compounds partially occupy both the M (16d) and rare earth (8a) sites [1-3]. The Curie temperatures T_C are considerably higher for the RNi$_2$Mn alloys in comparison with T_C for corresponding binary RNi_2 and RMn_2. Later, the structure and magnetic properties of the non-stoichiometric RM_2Mn_x ($0 \leq x \leq 1.5$) compounds with R = Tb, Dy, Gd were studied [4-7]. It was shown that the $MgCu_2$-type structure exists up to the manganese content $x = 0.8$ for $ErCo_2Mn_x$ and up to $x = 1.5$ for $ErNi_2Mn_x$. It was established that T_C is a non-monotonous function of Mn concentration, which has a maximum at $x < 1$. It was found also that the maximum isothermal entropy change and the adiabatic temperature change remain weakly changed in a wide temperature range in $ErCo_2Mn_x$. Thus, there is new opportunity to modify magnetic properties of the Laves phase compounds by adding Mn and forming non-stoichiometric RM_2Mn_x compounds.

Up to now the properties of $RM_2M`_x$ – type compounds with $M`$=Mn were studied only. However, we expect that non-stoichiometric $RM_2M`_x$ compounds with another 3d transition metals can exist. In particularly, such type compounds can forms in case $M`$=Ni.

In the present paper, we report the results of studies of the structure, magnetic and magnetothermal properties of the non-stoichiometric $TbCo_2Ni_x$. The obtained results are compared with those for $ErCo_2Mn_x$ which we previously studied.

2 Experimental details

The ingots of the $TbCo_2Ni_x$ alloys were prepared by induction melting of the constituents in alumina crucibles in argon atmosphere. In order to obtain the equilibrium phase state, the ingots were annealed at 800^{o}C for 7 days. Structural and magnetic studies were performed at the Centre of Collective Use of the Institute of Metal Physics UB RAS. Room temperature X-ray diffraction patterns were measured for powdered samples with the average particle size 30–50 μm using a DRON-type diffractometer with Cr Kα radiation. The x-ray diffraction patterns were analysed with the PowderCell 2.4 program. To determine the Curie temperature of the compounds, we measured temperature dependences of ac magnetic susceptibility χ_{ac} and used the position of minimum in the temperature dependences of derivative $d\chi_{ac}(T)/dT$, which corresponds to the more abrupt decrease in the susceptibility with increasing temperature. The spontaneous magnetization μ_s of compounds was determined from the demagnetization curves as magnetization extrapolated to zero internal field.

3 Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns of $TbCo_2Ni_x$ alloys. All main reflections in the X-ray diffraction patterns are adequately described in terms of the $MgCu_2$-type structure ($Fd3m$); the volume fraction of impurity phases with the $PuNi_3$-type structure ($R3m$) does not exceed 8 vol. %. According to X-ray diffraction studies, the single phase non-stoichiometric $TbCo_2Ni_x$ compounds with the cubic Laves-phase structure exist up to critical nickel concentration $x = 0.1$ [8]. This value is much lower than x = 0.8-1.5 which

* Corresponding author: inishev@imp.uran.ru

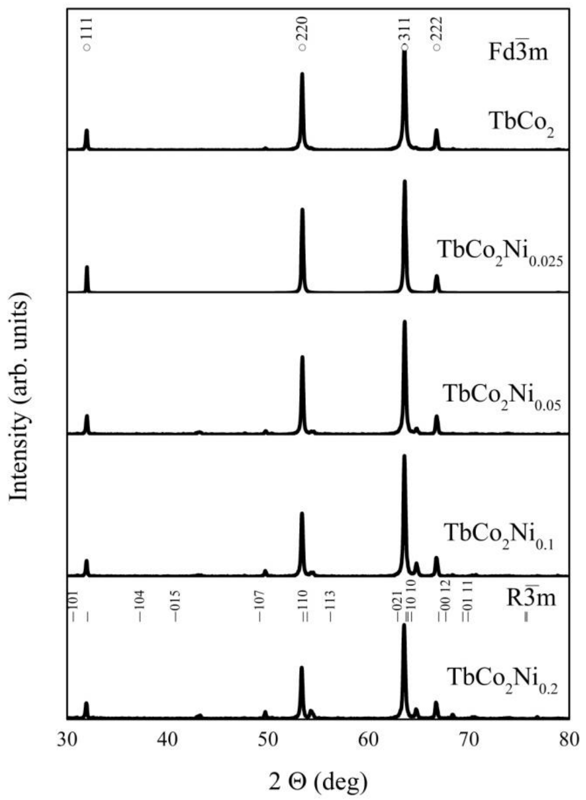

Fig. 1. X-ray diffraction patterns of $TbCo_2Ni_x$ alloys with different x. Bragg peak positions are indicated by the markers for $MgCu_2$-type structure (open circles). $PuNi_3$-type structures (line bars).

were observed early for non-stoichiometric RM_2Mn_x compounds. It is known that the stability of the Laves phases is determined by factors such as the relationship of atomic radii of R and M elements and the average number of valence electrons per atom. The chemical bonds in Laves phases are assumed to be mixed metallic–covalence–ionic. Because of this, to analyse the stability of the phases, atomic radii of elements are sometimes used. It is likely that the same factors must affect the concentration boundaries of the existence of the nonstoichiometric compounds. This may be due to that the atomic and ionic radii of Ni are less than those of Mn. And, correspondingly, large difference between Ni and R does not allows to occupy enough amount of R (8a) sites by Ni atoms. Thus, the non-stoichiometric RCo_2Ni_x alloys with cubic $MgCu_2$-type Laves phase structure can be obtained in more narrow concentration range than in case of alloying with Mn.

The lattice parameter of the Ni-containing compounds are virtually independent of x (Fig. 2). Such behavior caused by two opposite factors. It is known that the atoms of the alloying element (Ni or Mn) occupy both the R (8a) and the M (16d) sites. The partial substitution of the R atoms by Ni or Mn at the 8a sites leads to decrease the lattice parameter. On the other hand, the substitution of the Co atoms at the 16d sites by a 3d element with a larger ionic or metallic radius leads to increasing of the lattice parameter. Two opposite tendencies lead to a weak concentration change of the lattice parameter for $RM_2M'_x$.

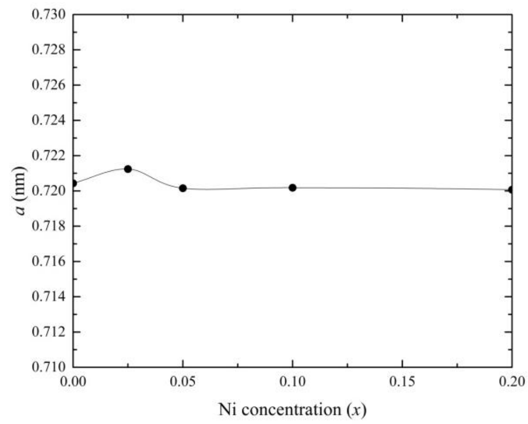

Fig. 2. Concentration dependences of the lattice parameter for $TbCo_2Ni_x$ compounds.

Fig. 3 shows the concentration dependences of the Curie temperature for $ErCo_2Mn_x$ and $TbCo_2Ni_x$ compounds in range of concentration from $x = 0$ up to maximal concentration for which exist single phase non-stoichiometric $TbCo_2Ni_x$ compounds with $MgCu_2$-type structure.

As can be seen in Fig. 3, concentration dependence of the Curie temperature increases sharply at small Ni concentrations and has maximum at $T = 233$ K. With further increasing the Ni content, the concentration dependence of the T_C decreases. The Curie temperature of $ErCo_2Mn_x$ compounds monotonically increases and reaches maximum value 212 K at manganese concentration $x = 0.6$ [6].

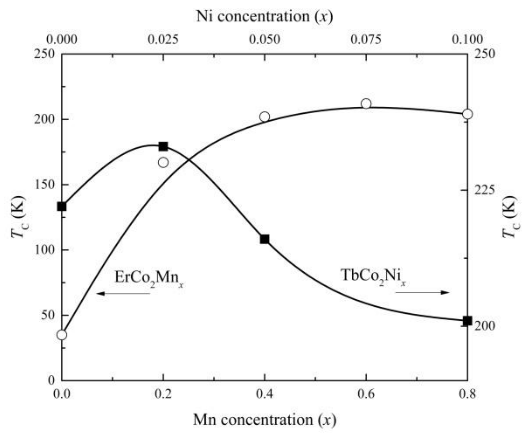

Fig. 3. Concentration dependences of the Curie temperature for $ErCo_2Mn_x$ (○) and $TbCo_2Ni_x$ (■) compounds.

The spontaneous magnetic moments μ_s decreases with increasing x both for $TbCo_2Ni_x$ and for $ErCo_2Mn_x$ as result of antiparallel ordering of magnetic moments of heavy rare-earth ions and 3d-transition atoms (Fig. 4).

Fig. 5 shows the concentration dependence of the magnetic moment of 3d-sublattice of $ErCo_2Mn_x$ and $TbCo_2Ni_x$ compounds. We calculated magnetic moment of 3d-sublattice μ_{3d} in assumption that the R and 3d magnetic moments have collinear antiparallel alignment:

$$\mu_{3d} = (\mu_R - \mu_s)/(2 + x), \quad (1)$$

where μ_s - spontaneous magnetic moment of the compounds, μ_R - magnetic moment of the rare-earth ion. The maximum μ_{3d} value is 1.38 μ_B for $TbCo_2Ni_{0.025}$ compound and 1.5 μ_B for $ErCo_2Mn_{0.6}$ compound. It is seen that character of the $\mu_{3d}(x)$ concentration dependencies both for $ErCo_2Mn_x$ and for $TbCo_2Ni_x$ is very similar to those for Curie temperatures.

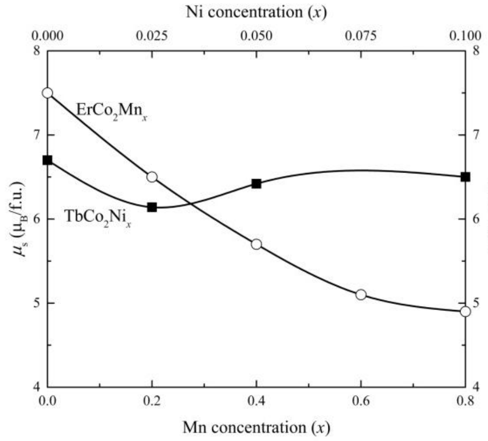

Fig. 4. Concentration dependences of the spontaneous magnetic moment at 4 K for $ErCo_2Mn_x$ (○) and $TbCo_2Ni_x$ (■) compounds.

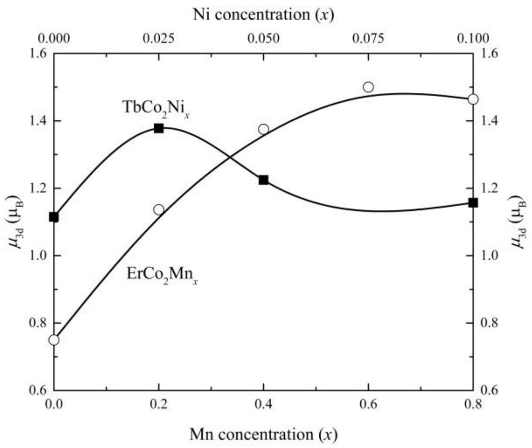

Fig. 5. Concentration dependences of the magnetic moment of 3*d*-sublattice for $ErCo_2Mn_x$ (○) and $TbCo_2Ni_x$ (■) compounds.

The $\mu_{3d}(x)$ dependence has maximum for $TbCo_2Ni_x$ and is monotonous for $ErCo_2Mn_x$. Our analysis of magnetic moments shows that the increase in the Curie temperature of the compounds is mainly due to changes in the band structure. It is possible, that alloying with Mn and Ni increase the Co magnetic moment due to the additional splitting of the 3d band. This, in turn, leads to an increase in the *R*-Ni (Mn), Co-Ni (Mn) exchange interaction.

We measured temperature dependences of magnetization $M(T)$ in magnetic field H_I = 1 T. It allows us to determine temperature variation of the magnetic entropy change $\Delta S_m(T)$ in $TbCo_2Ni_x$ compounds for magnetic field change $\mu_0\Delta H = H_I - 0 = 1$ T using well known Maxwell`s thermodynamic relation:

$$\Delta S_m(T, \Delta H) = \int_0^{H_1} \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \approx \frac{\partial M(T,H_1)}{\partial T} H_1. \quad (2)$$

Fig. 6 shows the temperature dependences of entropy change for $ErCo_2Mn_x$ and $TbCo_2Ni_x$ compounds. Maximum isothermal entropy change is -1.1 J kg^{-1}K^{-1} for $TbCo_2Ni_{0.025}$ and -1.15 J kg^{-1}K^{-1} for $ErCo_2Mn_{0.2}$ for the magnetic field change 1 T. These values are close to those observed, for the binary $TbCo_2$-based compounds.

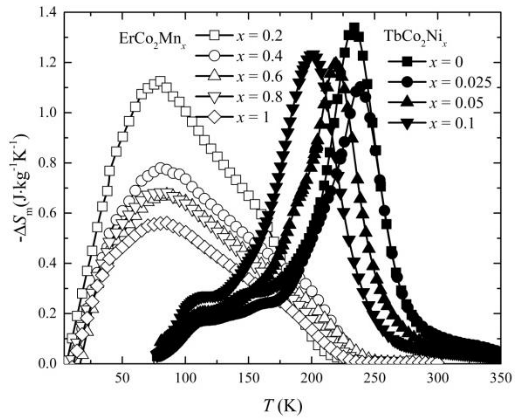

Fig. 6. Temperature dependences of entropy change of $ErCo_2Mn_x$ and $TbCo_2Ni_x$ compounds for magnetic field change $\mu_0\Delta H$ = 1 T.

The magnitudes of $\Delta S_m(T)$ decrease with increasing *M`* concentration because of decreasing the spontaneous magnetic moment of compounds. The behaviour of the $\Delta S_m(T)$ curves strongly differs. For $TbCo_2Ni_x$, $\Delta S_m(T)$ curves have maximum near T_C whereas, for $ErCo_2Mn_x$ maxima are observed at temperatures which are much lower than T_C. Such difference arises because $\Delta S_m(T)$ shape depends on shape of temperature dependence of resultant magnetization which reflects a non-Brillouin behavior of the resultant magnetization of the ferrimagnetically ordered *R* and *M*(*M`*) magnetic sublattices.

4 Conclusion

We studied the effect of Ni alloying on the structure, magnetic and magnetothermal properties of $TbCo_2Ni_x$ alloys. It was established that single-phase non-stoichiometric compounds with the cubic $MgCu_2$-type structure are formed at the Ni content $x \leq 0.1$.

We found that concentration dependences of the Curie temperature and magnetic moment of 3d-sublattice have maximum at Ni content x = 0.025. Our analysis shows that all these changes are associated with changes in the Co magnetic moment which can arise from changes of compounds electron band structure.

Using magnetization measurements, we estimated the magnetocaloric effect in the $ErCo_2Mn_x$ and $TbCo_2Ni_x$ compounds. The maximum values of the ΔS_m of $TbCo_2Ni_x$ compounds are sufficiently close for all nickel concentrations.

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